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TITLE OF THE INVENTION

Treating particulate alkaline earth metal carbonates

BACKGROUND OF THE INVENTION

(a) Field of the invention

The present invention relates to a method of treating a particulate material comprising an alkaline earth metal carbonate. In particular, the present invention relates to the treatment of such a material by heating with a surface treatment agent comprising a fatty acid.

(b) Known prior art

In the manufacture of particulate carbonate materials such as calcium carbonate for use in a variety of applications it is conventional to refine and treat the carbonate, eg obtained from a natural source such as marble, limestone or chalk, to provide suitable product properties by processing techniques such as milling, grinding and chemical treatments. Where the product is to be employed in applications in which it is to be incorporated in an essentially hydrophobic host material, eg a hydrophobic polymeric binder, the treated product is often coated with a surface treatment agent comprising a fatty acid or a salt or ester thereof which will render the surfaces of the particles of the product more suitable for incorporation in the hydrophobic host.

In the prior art various treatment methods have been employed to coat a carbonate containing particulate material with a hydrophobising surface

treatment agent, the method chosen depending on the nature of the agent employed.

Thus, some methods have involved treating the particulate material in an aqueous medium, especially where other processing steps applied to the material take place in an aqueous medium. Other methods have involved contacting the particulate material with the agent in a heated atmosphere, often whilst the particulate material is drying. The present invention is concerned with contacting the particulate material with the surface treatment agent in a heated atmosphere. The agent concerned comprises one or more fatty acids which are more reactive and generally less expensive than derivatives thereof and, which, because of their lower melting point and when applied in this way may be applied more easily and more cheaply.

We have found that where the surface treatment agent is applied by known prior art treatments, the amount of reaction between the surface treatment agent and the particulate product may not be ideal such as to render the particulate product fully or suitably hydrophobic. Alternatively, or in addition, where the treatment agent comprises one or more acids, the level of unreacted surface treatment agent associated with the treated product can be unduly high and this can cause problems when the product is used in an application in which it is incorporated in a hydrophobic composition comprising a polymeric binder material. Such a composition usually employs one or more various additives such as lubricants,

stabilizing agents, coloring agents, plasticizers, antistatic agents, anti-oxidants and metal passivating agents and the unreacted free acid can migrate and produce unwanted chemical reactions with one or more of such additives and/or unwanted deposition of material on processing equipment leading to a degraded processing method or product performance.

SUMMARY OF THE INVENTION

The purpose of the present invention is to provide a method of surface treating a particulate material comprising an alkaline earth metal carbonate with a surface treatment agent comprising a fatty acid, whereby the amount of surface treatment agent chemisorbed by the particulate material is controlled to give a sufficiently hydrophobic coating on the particles of the particulate material and whereby the amount of unreacted surface treatment agent may be minimized.

According to the present invention there is provided a method of treating a particulate material comprising particles of an alkaline earth metal carbonate which method includes the step of exposing the particulate material to a treatment atmosphere containing a surface treatment agent comprising one or more fatty acids which reacts with and coats the particles of the particulate material, wherein the treatment atmosphere is substantially water free and maintained at a temperature of at least about 120°C, preferably greater, and wherein in the treatment

atmosphere the concentration of the surface treatment agent available to contact the particulate material and the residence time of the particulate material are such as to provide a chemisorbed coating of the surface treatment agent on at least 75% of the surface area of the particulate material and the amount of physisorbed or unreacted surface treatment agent contained on the particulate material immediately after leaving the treatment atmosphere is not greater than about 0.5% by weight based upon the dry weight of the particulate material.

We have found surprisingly that in a method of the form described the use of a temperature of at least about 120°C, preferably at least 125°C, to coat the particles of the particulate material with the surface treatment agent allows a more efficient and more uniform (chemisorbed) bonding of the acid molecules of the surface treatment agent to the surface of the particles to be achieved compared with prior art treatments and, in consequence, the amount of free, unbonded (physisorbed) surface treatment agent, ie free acid, on the particles can be minimized thereby giving a coated particulate material product of improved quality. This improvement is further demonstrated hereinafter.

The temperature in a conventional method for the treatment with a surface treatment agent of a particulate material comprising an alkaline earth metal carbonate does not normally significantly exceed about 100°C-110°C since the surface treatment agent is normally applied whilst the particulate

material is in a wet or drying state and the presence of water vapour or steam produced by drying and the atmospheric pressure which normally exists limits the effective treatment temperature and/or the ability of the surface treatment agent to coat the carbonate particles.

DESCRIPTION OF THE INVENTION

The surface treatment agent used in the method according to the present invention may comprise one or more of the fatty acids comprising surface treatment agents employed in the prior art to treat alkaline earth metal carbonates. The said fatty acid may for example be one or more aliphatic saturated monocarboxylic acids having at least 8 chain carbon atoms, eg from 10 to 26 chain carbon atoms, eg selected from capric acid, lauric acid, montanic acid, myristic acid, palmitic acid, stearic acid, behenic acid, isostearic acid and cerotic acid and mixtures of two or more of these acids. Commercially available material may consist of mixtures. For example so called technical grade stearic acid consists of about 60%-65% by weight stearic acid and about 40%-35% by weight palmitic acid. Commercially available behenic acid may contain about 85%-90% behenic acid and minor amounts of other acids such as stearic, arachidic, lignoceric and palmitic acids.

The alkaline earth metal carbonate may comprise a carbonate of calcium, magnesium, barium or strontium or a carbonate of two or more alkaline earth metals, eg obtained from dolomite. The method

of the present invention is especially applicable to treat calcium carbonate-containing and magnesium carbonate-containing particulate materials. The calcium carbonate-containing material may have been produced in a known way from marble, chalk, limestone or dolomite. The magnesium carbonate may have been produced from magnesite.

The present invention is also applicable to treat alkaline earth metal carbonates which have been produced synthetically, eg calcium carbonate produced as a precipitate by reaction of calcium hydroxide and carbon dioxide in a known way.

Desirably, at least 95%, preferably at least 99%, by weight of the inorganic particulate material to be treated by the method of the invention comprises alkaline earth metal carbonate although minor additions of other optionally pre-treated mineral additives, eg one or more of kaolin, calcined kaolin, wollastonite, bauxite, talc or mica, could also be present together with the carbonate. Preferably at least 99% of the alkaline earth metal carbonate is calcium carbonate which may be obtained in a well known way by processing naturally occurring calcium carbonate obtained from a mineral source or by chemical synthesis, eg from the reaction of carbon dioxide and lime (calcium hydroxide). The present invention is particularly suitable to treat ground and processed calcium carbonate obtained from a mineral source.

The inorganic carbonate containing particulate material to be treated by the method of the invention

may have one or more of the following particle size properties:

(i) a median particle size (approximately equal to the value d_{50} defined below) of from 0.5μm to 10μm, especially from 0.5μm to 5μm, (eg) from 0.8μm to 3μm;

(ii) a particle size distribution steepness factor, ie $d_{50} \div d_{20}$, where d_{50} is the particle size value less than which there are 50% by weight of the particles, and d_{20} is the particle size less than which there are 20% by weight of the particles, of less than 2.2, desirably 1.1 to 2.2;

(iii) a top cut (the particle size value less than which at least 99% by weight of the particles of the material have a size) of less than 12μm, desirably less than 10μm;

(iv) a dispersibility as measured by Hegman gauge value, of 20μm or less, desirably 13μm or less;

(v) a specific surface area of from $3m^2.g^{-1}$ to $13m^2.g^{-1}$, especially from about $4m^2.g^{-1}$ to about $8m^2.g^{-1}$, as measured by the BET nitrogen absorption method.

All particle size values as specified herein are measured, unless stated otherwise, by the well known standard method employed in the art of sedimentation of the particles in a fully dispersed state in an aqueous medium using a SEDIGRAPH 5100 machine as supplied by Micromeritics Corporation, USA.

Dispersibility may be measured in a manner well known to those skilled in the art using the standard procedure specified in ISO 1524 using as test medium a long-oil alkyd resin with a 68% oil content of

vegetable fatty acids, SYNOLAC 60W made by Cray Valley Ltd.

In the method of the present invention the inorganic particulate material may comprise material which has been subjected to wet or dry processing in one of various well known ways to process the particulate material, eg to convert coarse, unrefined carbonate material obtained from a mineral source to a suitably pure and refined state. The material resulting from this processing may for example have a particle size distribution such that at least 60 per cent by weight, eg at least 70 per cent by weight of the particles of the material have an esd (equivalent spherical diameter measured by the known technique of sedimentation) of less than 2μm.

The particulate material treated in accordance with the present invention may have been subjected to the following treatment steps prior to treatment by exposure to the said surface treatment agent:

(a) preparation and/or processing of the particulate material in an aqueous medium;

(b) drying of the particulate material.

The processing of step (a) which may have been applied to the material may comprise one or more wet processing steps applied to refine and process the particulate material in a conventional manner. For example, the wet processing step may include grinding and/or milling and/or particle size classification.

The wet processed particulate material so treated may following such processing be washed and dewatered in a known way, eg by filtration or forced

evaporation, prior to drying, step (b) as referred to earlier. The drying step (b) may be carried out by heating in a hot atmosphere or current of air.

Alternatively, the material may have been subjected to dry processing eg using milling followed by grinding in a dry grinding mill, eg of the kind described in EP-A-0681155, prior to treatment with the surface treatment agent.

The exposure of the carbonate containing particulate material to the surface treatment agent may be carried out in a water dry treatment atmosphere containing the agent as a liquid (eg as droplets) and/or vapour in a treatment vessel heated externally, eg by a heating jacket, eg containing a heating fluid, eg a heating oil. Desirably, the carbonate containing particulate material enters the treatment vessel in the above described dry state and preferably also in a pre-heated state, eg heated to a temperature of at least 80°C, preferably at least 90°C, immediately prior to entering the treatment vessel. Such a temperature may result from the temperature applied in a drier prior to delivery of the particulate material to the treatment vessel, the material remaining at an elevated temperature between the drier and the treatment vessel.

Desirably, the temperature of the atmosphere in the treatment vessel can be externally varied and controlled so that a selected atmosphere reaction temperature may be chosen and monitored. The vessel may comprise an elongated heated cylindrical structure. Desirably, the required temperature is

maintained throughout the region where the surface treatment agent is applied and on exit from that region at a temperature of at least, preferably greater than, about 120°C.

Particulate material may be delivered for treatment in the treatment vessel in a batch or continuous process. For example, the particulate material may be conveyed into and out of the vessel in a current of hot air or other gas inert to the reagents employed.

The particulate material may be exposed to the surface treatment agent at a temperature of 120°C or more for a period greater than a minimum for effective treatment at a given feed rate of particulate material for the treatment equipment employed. For feed rates of between 2 tons per hour (1814 kg per hour) and 10 tons per hour (9070 kg per hour) the minimum residence time may for example be between 500 seconds and 100 seconds.

The average temperature at which the particulate material is treated with the surface treatment agent may desirably be a temperature in the range 125°C to 300°C, especially 125°C to 150°C. The higher temperature selected in the method of the invention provides sufficient heat to ensure good mobility of the molecules of the surface treatment agent and therefore good contacting of and reaction with the particles of the particulate material.

The treatment conditions are controlled so that the amount of unreacted surface treatment agent associated with the particulate material following

treatment in accordance with the method of the present invention is not greater than 0.5%, desirably not greater than about 0.4% by weight, and in some cases as low as 0.2% by weight or less, based on the weight of the uncoated particulate material. The amount of physisorbed or unreacted surface treatment agent may be measured accurately by the known analytical method of thermo-gravimetric analysis (TGA).

The treatment of the particulate material with the surface treatment agent is desirably carried out in a heated vessel in which a rapid agitation or stirring motion is applied to the atmosphere containing the particulate material and the surface treatment agent whilst in the vessel, whereby the surface treatment agent is well dispersed in the treatment atmosphere. Preferably, the agitation is not sufficient to alter the surface area of the particulate material for the reasons discussed later. The vessel may include for example one or more rotating paddles, comprising a rotating shaft having laterally extending blades comprising one or more propellers which ensure agitation and deagglomeration of the particles and intimate contacting of the particulate material with the surface treatment agent. The residence time of the particulate material in the vessel is sufficient to give the required reaction between surface treatment agent and particles being treated. This time may generally be greater than 2 seconds, eg at least 10 seconds. For example the residence time in many cases may be 50

seconds to 1000 seconds, eg 100 seconds to 500 seconds.

Desirably, the amount of surface treatment agent which is present in the heated atmosphere in which the particulate material is to be contacted by and treated with the surface treatment agent is not substantially greater than the maximum theoretical amount of the agent which can become bonded to or chemisorbed by the particulate material. This maximum theoretical amount is dependent on the surface area of the particulate material which, as noted above, preferably does not change during the coating process. The maximum theoretical amount of surface treatment agent required can be calculated as follows.

The theoretical surface coverage S by the surface treatment agent is given by the equation

$$S = M_a.N.A_a \qquad (1)$$

where M_a is the number of moles of the surface treatment agent present, A_a is the surface area occupied by 1 molecule of the surface treatment agent, and N is Avagadro's number. Using Equation (1) it can be shown in a first example that 1g of technical grade stearic acid (~65% by weight stearic acid and ~35% by weight palmitic acid) covers about 460 m^2 of the surface of a particulate alkaline earth metal carbonate. Thus, for such a particulate material having a surface area of about $5m^2.g^{-1}$ (as used in Examples described below and as measured by

BET) about 0.01g of surface treatment agent is required to give complete coverage of the surface of each 1g of the particulate material. Thus, the required theoretical maximum concentration of the surface treatment agent is about 1.0% based on the weight of the particulate material to be treated. In practice, the amount of surface treatment agent which becomes bonded to (ie chemisorbed onto) the particulate material may be less than the theoretical maximum, although by carrying out the surface treatment at a higher temperature in accordance with the present invention the coating process can be carried out more efficiently and the amount can approach more closely the theoretical maximum and the amount of undesirable unreacted surface treatment agent remaining can thereby be minimized giving a surprising and beneficial reduction in the amount of unreacted agent present on the resulting coated product.

In another embodiment, it can be shown that where the surface treatment agent is commercially available behenic acid, about 1.2% by weight of the surface treatment agent is the theoretical amount required to cover and treat the surface area of a particulate alkaline earth metal carbonate having a surface area of about $5m^2.g^{-1}$.

Desirably, the concentration of surface treatment agent present in the treatment atmosphere is from about 0.8X to about 1.2X where X is the theoretical minimum weight of surface treatment agent required to cover the surface area of the particulate

material, ie to produce a monolayer chemisorbed coating of the surface treatment agent.

Preferably, of the surface treatment agent on the resulting coated particulate material, eg immediately after leaving the treatment atmosphere, at least 80% by weight, preferably at least 85% by weight is chemisorbed, the remainder, if any, being physisorbed.

The surface treatment agent when added to the treatment vessel may comprise flakes or particles of a solid which becomes molten, fluid and well dispersed in the treatment atmosphere of the vessel through which the particulate material is passed as described above. For example, where technical grade stearic acid is employed this material as added to the inlet to the vessel may comprise irregular flat particles having sizes of from about 1mm to about 5mm.

Metered amounts of the surface treatment agent as a solid material may be added to the vessel via a feed hopper and an entry different from the entry of the particulate material. In a continuous process, the required amount may be added continuously to give delivery of the optimum amount of surface treatment agent in the treatment vessel as determined in the manner described above.

Desirably, the surface treatment agent does not contact the carbonate containing particulate material until the particulate material is in the treatment vessel whereby the particulate material can be suitably receptive to be coated by the surface

treatment agent and the concentration of the surface treatment agent to which the particulate material contacts can be controlled in order to maximise the amount of the agent chemisorbed onto the particulate material and to minimise the amount of unbonded or physisorbed agent for the reasons discussed later.

In use of the method according to the present invention, the particulate material which has been treated with the said surface treatment agent may optionally be further treated with one or more additional surface treatment agents, eg a known hydrophobic coupling agent such as an organosilane, organotitanate or zircoaluminate.

The particulate material treated in accordance with the method according to the present invention may be employed in a known manner as a pigment, filler, extender or property modifier in a composition (herein called an "application composition" comprising a hydrophobic or oleophilic material, eg comprising a resin or organic polymeric binder. The particulate material may be employed together with other inorganic particulate material selected from known pigment, filler, extender and property modifier materials conventionally employed as additives in compositions comprising hydrophobic or oleophilic compositions, for example, optionally pre-treated kaolinitic clay, calcined kaolinitic clay, mica, talc, aluminium silicate, including natural aluminium silicates such as feldspar and nepheline syenite, calcium silicate, including natural calcium silicates such as wollastonite,

bauxite, alumina trihydrate, hydroxide of magnesium, calcium sulphate, titanium dioxide, or a mixture of any two or more of these.

The polymeric material to which the particulate material is added to form an application composition may be of any of the kinds of hydrophobic or oleophilic (substantially water insoluble) polymeric materials in which inorganic particulate materials are known to be incorporated, eg as pigment, filler, extender, property modifying, reinforcing or coating materials. Such material may comprise for example a continuous polymer matrix when the filler is added therein or thereto, eg a shaped article. Such material may comprise a thermoplastic material, a thermosetting material, a cold setting material or a non-water based resin or resinous composition. Such materials may be employed in a variety of well known applications, eg as moulded plastics products, elastomers, rubbers, sealants, adhesives, varnishes, paints and the like. The particulate material may be added to the polymeric material to be distributed throughout the bulk thereof in a known manner. Alternatively, it may be added to the polymeric material in only a region thereof, eg on a surface of the material, eg where the material comprises a body to be coated.

The treated particulate material may be incorporated directly into or added to a body of a polymeric material to form a product by one of the suitable product forming processes well known in the art. Alternatively, the particulate material may be

formed together with thermoplastic or thermoplastic forming material into an intermediate product, eg as described in US 4,803,231 or WO 95/17441, such as in a granular or pellet form, which may subsequently be added to a polymeric, eg thermoplastic material for the formation of a product. Any of the polymeric materials described in US 4,803,231 or WO 95/17441 may be employed for this purpose. In particular, the particulate material may be formed into an intermediate product together with polyolefin materials, eg an amorphous or wax material, such as a polypropylene or a polypropylene/polyethylene co-polymer. Other known agents, eg lubricant, may be included in the intermediate product formation.

Examples of thermoplastic materials into which the particulate material treated by the method of the present invention may be incorporated with or without the formation of an intermediate product include polyolefin homopolymers or copolymers (eg low density or high density polyethylenes, linear polyethylenes, polypropylenes, ethylene-propylene copolymers, ethylene(vinyl acetate) copolymers, and ethylene-(acrylic acid) copolymers, halogenated polyethylenes (such as chlorinated polyethylene), polybutene, polymethylbutene, polyisobutylene, polystyrenes and polystyrene derivatives (eg SB, ABS, SA and SBS rubbers), PVCs, polycarbonates, polysulphones, polyether sulphones, PEEK, saturated polyesters (eg polyethylene terephthalates and/or polybutylene terephthalates), and polyphenylene oxides and blends, mixtures or copolymers containing these species.

We have found that the treated carbonate material produced by the method according to the present invention is especially suitable for incorporation into thermoplastic polyolefin compositions, especially containing polyethylene and polypropylene homo- or co-polymers.

As demonstrated later, by producing a carbonate containing particulate material by the method of the invention improved properties are obtained for the surface coated material. For example, the material may surprisingly and beneficially comprise a free-flowing hydrophobic powder having low moisture pick up and low tendency to produce agglomerates. It is very suitable to use as a mineral filler for use in thermoplastic, eg polyolefin resin compositions.

As noted above, where the application composition comprises a thermoplastic material the product-forming process employed to form a product from the thermoplastic material and the particulate filler material added thereto either as a powder or in the form of a granular or pelletised intermediate product as referred to above may be one of the methods well known in the art. Examples include melt compounding followed by extrusion of films, tubes, shapes, strips and coatings onto other materials, eg paper, metal sheet foil, injection moulding, blow moulding, casting and thermoforming. The melt compounding may for example be carried out in a suitable compounder or screw extruder. The thermoplastic material to be compounded may suitably be in a granular or pelletised form. The temperature

of the compounding and moulding, shaping or extrusion processes will depend upon the thermoplastic material being processed and materials incorporated therein. The temperature will be above the softening point of the thermoplastic material. Where the polymeric material comprises a non-thermoplastic material, eg thermosetting or cold setting resin it may be processed with incorporation of material according to the second aspect in a known way.

The application composition may include 1% or more, eg up to about 80% by weight, in particular usually from 10% up to 75% by weight, of the particulate material produced by the method of the present invention the amount depending upon the materials involved and the application of the product.

The application composition may include one or more optional additives well known to those familiar in the art, eg processing agents, such as lubricants, thermal or photochemical stabilising agents, colouring agents, plasticisers, antistatic agents, fire retardants, anti-oxidants, metal passivating agents or other reinforcing or filling agents such as natural or artificial fibres, metal particles, strands or foils, glass beads or microspheres and the like or other mineral (inorganic) fillers.

The application composition may be formed into products either alone or together with other materials such as plastics, metals, refractories, wood, paper etc. in the form of laminates, coatings and the like.

The inorganic particulate material surface coated by the method of the invention will be referred to as the "instant filler". The instant filler has been found to work extremely well as a mineral filler in producing intermediate product so called 'masterbatch' compositions together with thermoplastic polymers and other optional ingredients, especially products made using polyolefin based polymers. End products produced from such compositions such as cast film, blown film, and extrusion coatings using the instant filler in such applications can show an especially superior dispersion and extrusion performance, particularly with respect to homogeneity and quality of the film produced. The instant filler may be incorporated into compositions for use in producing film products at filler solids loadings ranging from 10% to as high as 75% and higher (by weight), while maintaining its ability to be processed into useful thin films, especially breathable films, using known processes, eg using cast or blown film, or extrusion coating processes.

A method of producing a porous, breathable film includes use in the film forming process of a composition which includes a thermoplastic polymeric material together with a filler, wherein the filler comprises partly or wholly the instant filler defined earlier.

The thermoplastic polymer may form from 10% to 70% by weight and the filler may form from 30% to 80% by weight of the composition, ie combination of the

polymer plus filler. The polymer preferably comprises more than 50% by weight of olefin units and is therefore usually referred to as a polyolefin resin.

The resins which can be used to provide the polyolefin resin to produce a composition suitable for producing films, for example, include mono-olefin polymers of ethylene, propylene, butene or the like, or copolymers thereof as a main component. Typical examples of the polyolefin resin include polyethylene resins such as a low-density polyethylene, linear low-density polyethylene (ethylene-α-olefin) copolymers, middle-density polyethylene and high-density polyethylene; polypropylene resins such as polypropylene and ethylene-polypropylene copolymer; poly(4-methylpentene); polybutene; ethylene-vinyl acetate copolymer; and mixtures thereof. These polyolefin resins may be obtained by polymerisation in a known way, eg by the use of a Ziegler catalyst, or obtained by the use of a single site catalyst such as a metallocene catalyst. Above all, polyethylene resins are preferable, and linear low-density polyethylene (ethylene-α-olefin) copolymers and low-density polyethylene are most preferable. Furthermore, in view of the mouldability, the stretchability and the like of the film, the melt index of the polyolefin resin is preferably in the range of about 0.5 to 5g/10 min.

Desirably, where one or more other fillers are employed together with the instant filler, the filler

includes at least 50% by weight, eg from 80% to 99% by weight of the instant filler.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

Embodiments of the present invention will now be described by way of example only with reference to the following Examples (in which prior art Examples are also included for the purpose of comparison).

EXAMPLE 1 (PRIOR ART)

A suspension was prepared containing 78% by weight of a particulate, calcium carbonate obtained from a natural marble source which had been comminuted by wet grinding to give a product having a particle size distribution such that about 90% by weight consisted of particles having an equivalent spherical diameter smaller than 2μm.

The suspension was then introduced into a hot gas swept attrition grinding mill of the type described in EP-A-0681155 and was ground and dried in the mill to the form of a fine, substantially aggregate-free powder.

The temperature of a heated vessel suitable for reacting technical grade stearic acid surface treatment agent with the dry calcium carbonate product in the manner described hereinbefore was adjusted to 220°F (104.4°C).

The vessel was provided as part of a Welex laboratory blending machine in which circulating oil could be employed to heat the vessel and up to about

2.2 kg of the calcium carbonate could be treated in a single batch.

The dried calcium carbonate product from the grinding mill was delivered into the vessel together with solid technical grade stearic acid and the two were allowed with vigorous stirring to contact and react together for a period of 2 to 3 minutes. The treated product extracted from the treatment vessel was collected by a bag filter. The concentration of surface treatment agent based on the weight of calcium carbonate present was 1.2 per cent by weight. The amount of unreacted stearic acid on the calcium carbonate particles was also measured after the treatment by high resolution thermogravimetric analysis and was found to be 1.0 per cent by weight. As a result, there were substantial agglomerates caused by unreacted acid in the specimen.

EXAMPLE 2 (INVENTION EMBODIMENT)

The procedure described in Example 1 was repeated. In this case, however, the temperature inside the reaction vessel was 250°F (121°C). The concentration of surface treatment agent employed was again 1.2 per cent by weight. In this case, with the higher reaction temperature the unreacted acid was found by thermogravimetric analysis to be only 0.5 per cent by weight of the calcium carbonate product.

EXAMPLE 3 (INVENTION EMBODIMENT)

The procedure described in Example 1 was again repeated. In this case however, the temperature

inside the reaction vessel was 300°F (149°C). The concentration of surface treatment agent was again 1.2 per cent by weight. In this case, with the reaction temperature raised further, the unreacted acid formed only 0.4 per cent by weight of the calcium carbonate product.

EXAMPLE 4 (PRIOR ART)

Ground, refined and dried calcium carbonate having a surface area of $5m^2.g^{-1}$ was treated with technical grade stearic acid at a concentration of 1.2% by weight (based on the weight of calcium carbonate) in a continuous and dynamic process in an industrial machine having a cascade of mixing propellers in a mixing vessel having a length of about 4m and a diameter of about 1.5m. Calcium carbonate powder was fed through the mixing vessel of the machine at a rate of about 7,200 $kg.h^{-1}$. Flakes of technical grade stearic acid surface treatment agent were added via a metering hopper to the atmosphere through which the powder passed in the mixing vessel so that the concentration of the surface treatment agent was 1.2% by weight. The temperature inside the vessel was 220°F (104.4°C). The surface treatment agent and calcium carbonate powder were intimately mixed in the mixing vessel by the propellers. The emerging product was collected in a bag filter and cooled and the amount of unreacted surface treatment agent was found to be (0.65±0.03)% by weight (based on the weight of calcium carbonate).

EXAMPLE 5 (INVENTION)

Calcium carbonate was treated with technical grade stearic acid (1.2 per cent by weight) in the manner described in Example 4, except that the treatment vessel temperature was 255°F (123.8°C). In this case, the amount of unreacted surface treatment agent was found by thermogravimetric analysis to be reduced to (0.41±0.03)% by weight (based on the weight of calcium carbonate).

EXAMPLE 6 (INVENTION)

Example 5 was repeated again using 1.2 per cent by weight of technical grade stearic acid, except that the treatment vessel temperature was 280°F (137.8°C). In this case, the amount of unreacted surface treatment agent was found by thermogravimetric analysis to be further reduced to (0.40±0.03)% by weight (based on the weight of calcium carbonate).

EXAMPLE 7 (PRIOR ART)

Example 4 was repeated again using a temperature of 220°F (104.4°C), except that the concentration of the surface treatment agent employed (technical grade stearic acid) was 1.0% by weight based on the weight of calcium carbonate. In this case, the amount of unreacted surface treatment agent was found by thermogravimetric analysis to be (0.58±0.03)% by weight based on the weight of calcium carbonate.

EXAMPLE 8 (INVENTION)

Example 7 was repeated again using 1.0 per cent by weight of technical grade stearic acid, except that the temperature of the treatment vessel was 255°F (223.8°C). The amount of unreacted surface treatment agent was found by thermogravimetric analysis to be reduced to (0.35±0.03)% by weight (based on the weight of calcium carbonate).

EXAMPLE 9 (INVENTION)

Example 7 was repeated again using 1.0 per cent by weight of technical grade stearic acid, except that the temperature of the treatment vessel was 280°F (137.8°C). In this case, the amount of unreacted surface treatment agent was found by thermogravimetric analysis to be further reduced to (0.32±0.03)% by weight (based on the weight of calcium carbonate).

EXAMPLE 10 (PRIOR ART)

Example 1 was repeated, except that the surface treatment agent was behenic acid (1.2 per cent by weight). The amount of unreacted surface treatment agent was found by thermogravimetric analysis to be (1.05±0.10)% by weight based on the weight of calcium carbonate).

EXAMPLE 11 (INVENTION)

Example 10 was repeated again using 1.2 per cent by weight of behenic acid as surface treatment agent, except that the temperature of the treatment vessel was raised to 300°F (149°C). In this case, the

amount of unreacted surface treatment agent measured by thermogravimetric analysis was reduced to (0.39±0.02)% by weight based on the weight of calcium carbonate.

The above Examples illustrate that the amount of unreacted surface treatment agent is unexpectedly and beneficially reduced by increasing the temperature of the surface treatment (of the alkaline earth metal carbonate by the surface treatment agent) above about 120°C in accordance with the present invention.

EXAMPLE 12 (COMPARATIVE)

Three sets (designated 1, 2 and 3) of fatty acid coated calcium carbonate samples were produced. Each set consisted of two samples, one prepared by coating refined calcium carbonate using a lower coating treatment temperature and another prepared by coating the same calcium carbonate under identical conditions but using a higher coating treatment temperature in a method embodying the invention. A summary of the samples produced is as follows.

Set No	Sample No	Coating acid	Coating treatment temperature (°C)
1	A	Acme Hardesty 60	110
1	B	Acme Hardesty 60	127
2	C	Industrene B	116
2	D	Industrene B	132
3	E	Commercial behenic acid	110
3	F	Commercial behenic acid	127

Acme Hardesty 60 is the trade name for a carboxylic acid blend containing about 60% by weight palmitic acid and about 40% by weight stearic acid.

Industrene B is the trade name for a carboxylic acid blend containing about 60% by weight stearic acid and about 40% by weight palmitic acid.

The Commercial behenic acid employed comprises about 90% by weight behenic acid and about 10% by weight of other fatty acids.

Mineral properties of Samples 1 to 6 were measured. Samples A to F were also melt compounded into resin based compositions using commercially available LLDPE resins. Blown and cast films were produced from these resin based compositions and properties of the resulting films were measured. The procedures employed to compound the Samples A to F and form films and also to investigate the properties of the Samples and their use in compounding and formation of cast and blown films were as follows.

Mineral Testing: The particle size distribution of the coated calcium carbonates Samples A to F after screening using a 325 mesh screen were measured in isopropyl alcohol on a MICROTRAC particle size analyzer using triple beam laser light diffraction techniques. The percentages of reacted and unreacted coating acid were measured on a TGA analyzer set to a temperature ramp of 5°C/min through a range of 20°C to 600°C. The unreacted acid was defined as weight loss between 150°C and 250°C, the reacted acid was defined as weight loss between 250°C and 500°C. The moisture pick up after 48 hours was measured by

placing the Samples of dried coated calcium carbonate (dried at 200°C) in a bell jar which was saturated at a 50% relative humidity over a sulfuric acid solution. After 48 hours the Samples were heated to 200°C and a weight loss calculated.

Compounding and film processing: The resin and filler in each case were mixed in a compounder having a screw speed of about 348rpm and throughput of about 13.5kg.hr^{-1} with a melt temperature of about 220°C.

For blown film processing the following operational parameters were employed: barrel melt temperature 421°F (260°C), rotational speed 50rpm, towerspeed 30rpm, adapter pressure ~2050psi (14.1MPa). For cast film processing the following operational parameters were employed barrel melt temperature 452°F (233°C), rotational sped 40rpm, barrel pressure ~1900psi (13.1MPa), tower speed 25rpm, adapter pressure ~1100psi (7.6MPa).

Blown film testing: The coated calcium carbonate Samples 1 to 6 were each separately compounded in a 1 melt index hexene LLDPE resin for physical property testing at a loading of 50% calcium carbonate by weight. This was let down in the same resin on a film line for a final film loading of 20%. Test samples were conditioned for 48 hours at 23°C, 60% relative humidity.

Tear strength was measured according to ASTM D 1922. Impact strength was measured on a Dynatup instrumented impact tester according to ASTM D 3763. Oxidation induction time (OIT) was measured by placing a 10mg pellet of compound in a differential

scanning calorimeter and heating the pellet to 190°C under nitrogen. Once the temperature was reached, the gas was switched to oxygen and the time until oxidation occurred measured.

Cast film testing: The coated calcium carbonate Samples 1 to 6 were each separately compounded in a 3 Melt Index octene LLDPE resin at a 50% loading level. The compound was made directly into film to determine if lensing would occur in the film with these calcium carbonates. Agglomeration levels were measured by macroscopically examining three 45cm^2 sections of film produced with the octene LLDPE resin and counting the number of visible particles/agglomerates.

The results which were obtained for these investigations are as follows.

(1) Particle size distribution of coated carbonates

Sample	%<1 micron % by weight	Median particle size (μm)	Top Cut (μm)
1	17.88%	1.58	11.0
2	18.23%	1.55	11.0
3	13.83%	1.73	6.5
4	15.19%	1.71	6.5
5	12.21%	1.84	7.8
6	11.56%	1.86	6.5

(2) Percentage of reacted (chemisorbed) coating acid (as a percentage of overall acid concentration)

Sample	% reacted acid (by weight)
3	79.7
4	83.0
5	76.7
6	92.1

(3) Moisture pick up of coated carbonates after 48 hours at 50% relative humidity

Sample	% moisture (by weight)
1	0.04
2	0.01
3	0.05
4	0.02
5	0.05
6	0.03

(4) Film properties

Sample No	Agglomerates per square centimeter
1	0.33
2	0.10
3	0.71
4	0.44
5	0.66
6	0.19

The tear strength and impact strength and OIT were substantially unaffected by the production method employed for the Samples.

The following conclusions can be made from the various comparative results given above. Use of a higher temperature for the fatty acid surface coating treatment shows the following benefits: (a) a higher percentage of reacted (chemisorbed) acid and consequently a lower amount of remaining unreacted

acid; (b) lower moisture pick up content; and (c) lower agglomeration levels in films. The significance of these benefits is as follows.

Unreacted Acid: Unreacted acid, ie coating acid that is not directly bonded to the surface of the calcium carbonate, is free to migrate during the compounding and converting processes. Evidence of this may be observed by unwanted deposition of material on processing equipment in the compounding and film forming processes. In addition, the presence of high levels of unreacted acid can cause unwanted oxidation of ingredients of the polymer composition during melt processing.

Agglomeration: Agglomeration of coated calcium carbonate before or during compounding can be a source of a number of types of defects or failures in preparation of a thermoplastic composition and films containing the carbonate. The agglomerates form as a result of a higher affinity of the carbonate for itself than the polymer into which it is being compounded. Evidence has been found which shows that this can be due to hydrophilic interactions of the carbonate due either to overcoating the stearic acid (ie an excess of physisorbed acid) or undercoating the acid such that there is not a complete monolayer coating of the surface.

Moisture Pick up: Low moisture pick up is desirable for coated calcium carbonates in application thermoplastic compositions especially for film applications in order to give improved processibility and product quality.

The higher temperature coated calcium carbonate Samples also showed that following beneficial properties: (a) better flowability; (b) better wetting of the calcium carbonate Sample by the LLDPE polymer, both because of the increased hydrophobicity of the material resulting from more complete chemisorbed coating of the particle surfaces and reduced unreacted acid.